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"IMPROVEMENTS IN OR RELATING TO THE PROCESS FOR THE SURFACE PREPARATION OF MANDRELS WITH NICKEL-TIN ELECTRODEPOSIT FOR ELECTRO FORMING ARTICLES"

COUNCIL OF ~~XXX~~ SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated under the Registration of Societies Act (ACT XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and SUBBIAH JOHN, Junior Scientific Assistant, both are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

PRICE: TWO RUPEES

This invention relates to the process for the electroforming of metal articles and has for its principal object the provision of means for facilitating stripping of such articles from the mandrel on which they are formed. This invention is particularly directed to facilitating the stripping of electrodeposited copper and nickel sheets and other electroformed articles from copper and other mandrels.

When a layer of copper or other metal is deposited upon a mandrel from which the deposit is subsequently to be stripped, that mandrel surface must be smooth and free from flaws and tarnishing. If this surface condition is not attained, the product will be damaged upon being stripped from the cathode. For example, the result of employing a flawed cathodic surface in the production of electrodeposited copper sheet is the presence of pinholes in the electrodeposited sheet or foil. A very irregular surface or the use of an unsuitable metal cathode can cause severe damage by virtue of large portions of the electrodeposited copper cohering to the cathode.

Heretofore lead, stainless steels, tantalum, tiatanium and mandrels coated with chromium, silver and rhenium has been used as mandrels in the production of sheet copper and other articles by the electrodeposition process. The surface o each of these metals is polished to a smooth finish and the deposited articles is quite easily removed.

But the commercial application of these mandrel materials frequently depends on variables other than the electrodeposition process environment. Thus, stainless steels, tantalum, tatanium Rhenium and chromium coated mandrels are costly. The manufacture of mandrels in the form most widely used for continuous electrodeposition operations (i.e. drum cathodes of large diameter) requires a large capital outlay. Moreover, stainless steel is hard and difficult to polish and to keep polished with an adequately smooth finish.

Lead is more widely used than stainless steels, but particles of lead from the mandrel commonly become included within the crystal lattice of the electrodeposited sheet. Thus, upon stripping, the copper material is slightly contaminated with lead. The degree of contamination is slight but sufficient in many cases to render the copper unsuitable for some important uses such as making printed circuits.

A copper mandrel is superior to all the above metals, but is subject to the disadvantage in that its surface possesses a high cohesive affinity for most metals that can be electrodeposited thereon Hence, it is hard to strip the electrodeposited metal from it without irreparably damaging the electrodeposited product, unless its surface is first prepared by an oiling procedure that is not practical for drum cathodes in the continuous production of electrodeposited sheet metal. Still another procedure is to coat the surface of the mandrel with an aqueous solution of benzotriazole. But this produces a brittle deposit due to its inherent stress giving characteristics.

This invention is based on our discovery that when a suitable mandrel is coated with a layer of nickel-tin alloy deposit prior to electroforming and when such a mandrel is used as a cathode in the electroformingbath, the electrodeposited metal is stripped with great case from the mandrel without injury to either the mandrel or to the electroformed article.

The present invention provides an improved electroforming process for the production of metal articles including copper and nickel sheet and electroformed copper and nickel articles wherein these items may be stripped with great ease from the madrel upon which they have been formed. Our invention permits stripoing of the metal from the mandrel surface without danger of damage to the product or irregular coherence of the electroformed metal to the mandrel.

These desirable achievements of our invention are accomplished by coating the mandrel surface with an electrodeposit of nickel-tin alloy prior to electroforming to provide a parting layer for the easy separation of the article. This parting layer is applied from an electroplating bath containing stannous chloride, nickel chloride, ammonium bifluoride, sodium fluoride, ammonium chloride, ammonium hydroxide upton a thickness of 0.002".

The following typical examples are given to illustrate the invention:

EXAMPLE 1

Copper mandrel of size 20 cms x 15 cms was prepared by the following sequence of operations: Preliminary pretreatment, rinsing, electrocleaning, rinsing, acid dipping, rinsing and electroplating in the following bath:

Stannous chloride	:	50 g/l
Nickel chloride	:	300 g/l
Ammonium bifluoride	:	56 g/l
Ammonium chloride	:	50 g/l
Ammonium hydroxide (0,880- Sp.gr.)	:	35 ml/l
pH (Colorimetric)	:	2.5
Cathode current density	:	2.4 A/dm^2
Current efficiency	:	100%
Temperature	:	68 $\pm$ 3°C
Anode	:	Separate Tin and nickel anodes
Thickness	:	50 microns
Time	:	One hr.

The composition of the alloy deposited was 65% tin and 35% nickel and the harness was 710 Vickers Diamond Pyramid number. The mandrel after applying the nickel-tin coating was smooth, shining and hard. The corrosion resistance properties of the coating in the industrial atmosphere is as good as that of chromium. The mandrel was used as a cathode in the conventional nickel and copper electroforming baths. The deposit was very easily separated from the mandrel and it is pore-free. The mandrel was used repeat y without any further treatment.

EXAMPLE II

Brass mandrels of size cms x 20 cms were polished, degreased, cleaned cathodically in a mix d sodium phosphate, metal silicate solution, acid dipped, rinsed and plated in the nickel-tin alloy bath of the composition given in Ex.1 to a thickness of 50 microns.The hardness of the deposit was 710 Vickers Diamond Pyramid No.

The nickel-tin alloy deposited mandrel was used as a cathode in the conventional copper and nickel electroforming baths. The deposit was very easily separated and it was pore-free. The mandrel was used again and again without any further treatment.

EXAMPLE III

Mild steel mandrels of size 15 cms x 20 cms was prepared before applying the nickel-tin alloy deposit by the following sequence of operations: Polished, degreased, cathodically cleaned in alkali, rinsed, pickled in 50% (by volume) hydrochloric acid for 30 seconds, cyanide copper strike rinsed, acid dipped, rinsed. It is then plated using the nickel-tin alloy plating bath given in Exa.1 to a thickness of 50 microns. The hardness of the deposit was 710 Vickers Diamond Pyramid No.

After applying the tin-nickel alloy deposit, the mandrel was taken to the conventional copper and nickel electroforming baths. The deposit was very easily separated and it was pore-free. The mandrel was used again and again without any further treatment.

EXAMPLE IV

All the above three types of mandrels mentioned in the previous examples are taken to the following nickel-tin alloy plating bath after the cleaning treatments:

Stannous chloride	:	50 g/l
Nickel chloride	:	300 g/l
Sodium fluoride	:	28 g/l
Ammonium bifluoride	:	35 g/l
Ammonium chloride	:	50 g/l
Ammonium hydroxide	:	as needed to pH2.0 -2.5 (colorimetric
Temperature	:	$65^{o} - 70^{o}C$
Current density	:	2.4 A/dm^2
Current efficiency	:	100%
Thickness	:	50 microns
Anode	:	Separate Tin and nickel anodes
Time	:	One hr.

The composition of the alloy deposit was 65%, tin, and 35% nickel and it was hard and shining. Properties are similar to Example 1. The mandrel was kept as the cathode in the conventional nickel and copper electroforming baths. The electroformed article was very easily separated without any injury to either the mandrel or to the article. The mandrel was used again and again without any further treatment.

EXAMPLE V

All the above cited mandrels after applying the nickel-tin alloy deposit was taken to the conventional iron electroforming bath. The deposit was very easily separated from the mandrel using nickel-tin alloy as the parting medium. The mandrel was used again and again without any futther treatement.

The following are the main advantages of the invention:

1 The mandrel prepared by this process is more economical and cheap.

2. The corrosion resistance properties of the coating is superior and hence the life of the mandrel is more.

3. The hardness is also high and this further increases the resistance for wear and tear during the separation of the article from the mandrel.

Dated this 20th day of March, 1975.

Sd/-
Asstt. Patents Officer,
Council of Scientific & Industrial Research

THE PATENTS ACT 1970

COMPLETE SPECIFICATION

SECTION 10

"IMPROVEMENTS IN OR RELATING TO THE PROCESS FOR THE SURFACE PREPARATION OF MANDRELS WITH NICKEL-TIN ELECTRODEPOSIT FOR ELECTROFORMING ARTICLES"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated under the Registration of Societies Act (ACT XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the xxxx manner in which it is to be performed :-

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and SUBBIAH xxxxx JOHN, Senior Technical Assistant, both are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi-623 006, Tamil Nadu, India.

Electroforming is the production or reproduction of articles by electrodeposition upon a mandrel or master that is subsequently separated from the deposit. Electroforming is a specialised application of the electroplating process. The electroform serves functionally as decoratively as a separate entity. Accordingly the mandrel or master is removed from the electroform. Mandrels used for electroforming are classified as permanent or expendable. Permanent mandrels are generally preferred for accuracy, and especially for high production runs, in which its intial cost can be spread over a number of pieces. Expendable mandrels of low melting point alloy may be used for producing a single piece, or for low cost items not requiring close tolerances. Expendable mandrels must be used whenever the part is so designed that permanet mandrels cannot be withdrawn.

This invention relates to the process for the electroforming of metal articles using permanent mandrel and has its principal object the provision of means for facilitating stripping of such articles from the mandrel on which they are formed. This invention is particularly directed to facilitating the separation of electroformed copper and nickel sheets and other electroformed articles from the mandrel.

When a layer of copper or nickel is deposited upon a permanent mandrel from which the deposit is subseqdently to be separated,that mandrel surface must be smooth and free from flaws and tarnishing. If this surface condition is not attained, the product will be damaged upon being stripped from the mandrel. With permanent mandrel steps must be designed to maintain a balance between complete activation and complete passivation of the surface, otherwise a parting medium must be used. Without a parting medium, too active a surface will result in strong adhesion that will prevent parting; too passive a surface may result in curling,exfoliation or splitting of the electroforms, especially if the deposit is highly stressed. A very irregular surface or the use of an unsuitable metal mandrel can cause severe damage by virtue of large portions of the electroform cohering to the mandrel. Hence not only the product is ruined but the mandrel surface itself must be cleaned and polished if it is to be used again.

Hitherto it has been proposed to use the following mentals as mandrel for electroforming applications:

a) Stainless steels, tantalum and titanium as such are used as permanent mandrel

b) Lead coated copper and steel mandrels

c) Chromium, silver and rhenium plated as a parting medium over permanent mandrel

The commercial application of these mandrel materials depeonds on variables other than the condition needed for electrodeposition. The main drawbacks associated with the hitherto known process are that:

a) mandrels made of stainless steels, tantalum and titanium are costly and the manufacture of mandrels in the form most widely used for continuous electroforming operations (i.e. drum cathodes of large diameter requires a large capital outlay. Moreover, stainless steel is hard and difficult to polish and to keep polished with an adequately smooth finish. Even in carefully prepared stainless steels, the presence of non conducting oxides which are not uniform result in preferential sites for nucleation of the deposit resulting in pinhole formations in the thin electroformed foils.

b) With the use of lead coated mandrel, particles of lead from the mandrel commonly become included within the crystal lattice of the electrodeposited sheet. Thus upon stripping,the electroformed copper foil is contaminated with lead. The degree of contamination is slight but sufficient in many cases to render the copper unsuitable for some important uses such as making printing circuits.

c) Silver, rhenium and chromium plated mandrels are costly and maintenance is bit difficult.

A copper mandrel is superior to all the above metals, but is subject to the disadvantage in that its surface possesses a high adhesion affinity for most metals that can be electrodeposited thereon. Hence, it is hard to separate the electrodeposited metal from it without irreparably damaging the electroformed product, unless its surface is first prepared by an oiling procedure which usually produces porous electroform. Still another procedure is to coat the surface of the mandrel with an aqueous solution of benzotriazole. But the use of benzotriazole produces brittle deposit due to its inherent stree developing characteristics.

The main object of the present invention is to obviate these disadvantages by using a simpler process for the surface preparation of mandrel based on mild steel, bras and copper which aids easy parting of the electro formed product from the mandrel on which they have been formed.

The main finding underlying the invention consists of the process of electroplating an initial layer of nickel-tin alloy on steel,brass and copper mandrel from an aqueous electrolysing bath comprising nickel chloride 250-300 g/l, stannous chloride 50 g/l, ammonium fluoride 35 g/l, ammonium bifluoride 35-55 g/l, ammonium chloride 50 g/l, sodium fluoride 30 g/l, ammonium hydroxide or hydrochloric acid or hydrofluoric acid to pH 2.0-2.5 at a temperature of 60-70^{o}C, at a current - - - - - - - - - - - - - - density of 2-4 A/dm^2 and then electroforming copper, nickel and iron from conventional electroforming baths over the mandrel as prepared above and finally separating or parting the electroformed article from the mandrel to form a separate entity.

The new result flowing from the new finding is that be provision of electrodeposited nickel-tin alloy over the mandrel enables easy separation of the subsequent electroformed articles from the mandrel without damage or irregular adherence of the electroform. The nickel-tin alloy deposited from the bath as per the invention is bright as deposited and thereby avoids further polishing. Hence, pore free electroformed articles can be produced from this type of mandrel produced according to this invention.

The flow-sheet of the process is given below:

Mechanical Polising and buffing of copper, brass or steel mandrel

↓

Degreasing with a solvent such as trichloro ethylene

↓

Cathodic cleaning in an alkaline solution

↓

Acid dipping

↓

Nickel-tin-alloy plating

↓

Electroforming of copper, nickel or iron

↓

Separating the electrofo med copper, nickel or iron article from the mandrel

(with intermediate washing between two consecutive steps)

The following typical examples are given to illustrate the invention:

EXAMPLE-1

Copper mandrel of size 20 cm x 15 cm was prepared by the following sequence of operations: Preliminary pretreatment, rinsing, electro-cleaning rinsing, acid dipping, rinsing and electroplating in the following bath:

Stannous chloride	:	50 g/l
Nickel chloride	:	300 g/l
Ammonium bifluride	:	55 g/l
Ammonium chloride	:	50 g/l
Ammonium hydroxide (0.880 - Spg. gr.)	:	to pH
pH (colorimetric)	:	2.5 (pH lowered with hydrofluoric acid)
Cathode current density	:	2.4 A/dm^2
Current efficiency	:	100 %
Temperature	:	68 ± 2^oC
Anode	:	Separate tin and nickel anodes
Thickness	:	50 microns
Time	:	1 hour

The composition of the alloy deposited was 65% tin and 35% nickel. It is an intermetallic compound corresponding to the composition NiSn, which is metastable and cannot be duplicated by thermal means. This intermetallic compound has surprising resistance to corrosion. Consequently, its resistance to attack by various chemical reagents and its corrosion under various conditions of atmospheric exposure is good. Separate anodes of nickel and tin are used in independently controlled circuits. When tin and nickel anodes are connected in paralle in the plating bath, the tin anodes dissolve about 20 times faster than nickel anodes. By making the area of the tin anodes only 1/20 that of the nickel anodes, the rate of dissolution of the two metals was made about equal, and a plating bath was successfully operated without significant change in composition. This bath can also be operated with nickel anodes and the tin content of the bath is replenished by additions of anhydrous stannous chlodie.

The hardness of the deposit was 710 Vickers Diamond Pyramid Number. The mandrel after applying the nickel-tin coating was smooth, shining and hard. The corrosion resistance properties of the coating in the industrial atmosphere is as good as that of chromium. The madrel was used as cathode in the conventional nickel or copper electroforming baths The deposit was very easily separated from the mandrel and it is pore-fr The mandrel was used repeatedly without any further treatment.

EXAMPLE-2

Brass mandrels of size 15 cm x 20 cm were polished, degreased, cathodically cleaned, acid dipped, rinsed and plated in the nickel-tin alloy bath of the composition given in Example 1 to a thickness of 10 microns. The hardness of the deposit was 700 Vickers Diamond Pyramid Number.

The nickel-tin alloy deposited mandrel was used as cathode in the conventional copper or nickel electroforming baths. The deposit was very easily separated and it was pore-free. The mandrel was used again and again without any further treatment.

EXAMPLE-3

Mild steel mandrels of size 20 cm x 15 cm were prepared before applying the nickel-tin alloy deposit by the following sequence of operations: Polished, degreased, cathodically cleaned in alkali, rinsed,pickled,given cyanide copper strike, rinsed, acid dipped and then rinsed.It is then plated using the nickel-tin alloy plating bath given in Example 1 to a thickness of 15 microns. The hardness of the deposit was 710 Vickers Diamond Pyramid Number. After applying the tin-nickel alloy deposit, the mandrel was taken to the conventional copper or nickel electroforming baths. The deposit was very easily separated and it was pore-free.The mandrel was used again and again without any further treatment.

EXAMPLE-4

All the three types of mandrels mentioned in the previous examples were taken to the following nickel-tin alloy plating bath after the cleaning treatments:

Stannous chloride	:	50 g/l
Nickel chloride	:	300 g/l
Sodium fluoride	:	28 g/l
Ammonium bifluoride	:	35 g/l

Ammonium chloride	:	50 g/l
Ammonium hydroxide or hydrofluoric acid	:	as needed to pH 2.0-2.5 (colorimetric)
Temperature	:	65-70°C
Current density	:	4 A/dm^2
Current efficiency	:	100%
Thickness	:	25 microns
Anode	:	Separate tin and nickel anodes
Time	:	18 minutes

The composition of the alloy deposit was 65% tin and 35% nickel and it was hard and shining. Properties are similar to Example 1. The mandrel was kept as cathode in the conventional nickel or copper electroforming baths. The electroformed article was very easily separated without any injury to either the mandrel or to the article. The mandrel was used again and again without ay further treatment.

EXAMPLE-5

All the above cited amndrels are taken to the nickel-tin alloy plating bath having the following composition after the cleaning treatments

Nickel chloride	:	250 g/l
Stannous chloride	:	50 g/l
Ammonium fluoride	:	35 g/l
Hydrochloric acid(32%)		to pH
pH	:	2.5 (adjusted with NH_4 CH/HCL)
Temperature	:	60-65°C
Current density	:	3.2.A/dm^2
Current efficiency	:	100%
Time	:	9 minutes
Thickness	:	10 microns
Anode	:	Nickel

The composition of the alloy deposited was 65% tin and 35% nickel and the hardness was 700 Vickers Diamond Pyramid Number. This bath was operated with nickel anode and the tin content of the bath was replenished by additions of anhydrous stannous chloride.The mandrel after applying the nickel-tin coating was smooth, shining and hard. The mandrel was then kept as cathode in the conventional nickel or copper or iron electroforming baths. The electroformed article was very easily separated from the mandrel without any injury to either the mandrel or to the article.

EXAMPLE-6

All the above cited mandrels after applying the nickel-tin alloy deposit were taken to the conventional iron electroforming bath. The deposit was very easily separated from the mandrel using nickel-tin alloy as the parting medium. The mandrel was used again and again without any further treatement.

The following are the main advantages of the invention:

1. In comparison with the widely used stainless steel mandrel,the mandrel prepared by this process is more economical and cheap
2. The parting layer deposited from the fluoride-chloride bath is bright as deposited and is resistant to chemical attack by the common reagents. This property eliminates the need for further polishing and also the brightness is also maintained for prolonged period. This further enables the production of pore-free electroformed articles.

A process for the production of electroformed articles which comprises preliminary surface preparation and cleaning of master or mandrel depositing a parting layer which is an alloy of nickel-tin prior to electroforming and electroforming from conventional baths wherein the nickel-tin alloy enables easy separation of electroformed articles from the mandrel.

WE CLAIM :

1. A process for the surface preparation of mandrels with nickel-tin electrodeposit for electroforming of articles which comprises the steps of mechanical polishing and buffing of copper, brass or steel mandrel, degreasing with a solvent such as trichloroethylene, electrolytic cleaning in an alkaline solution, acid dipping and subsequent plating of nickel-tin alloy deposit from an aqueous solution containing nickel chloride 250-300 g/l, stannous chloride 50 g/l, ammonium fluoride 35 g/l, ammonium biflurodie 35-55 g/l, ammonium chloride 50 g/l, sodium fluoride 30 g/l, ammonium hydroxide or hydrochloric acid or hydrofluoric acid to pH 2.0-2.5 at a temperature of 60-70^{o}C, at a current density of 2-4 A/dm^2 and then electroforming copper, nickel and iron from conventional electroforming baths on the mandrel as prepared above and finally separating or removing the electroformed article from the mandrel.

Dated this 17th day of May 1976.

Sd/-R.Bhaskar Pai,
PATENTS OFFICER
Council of Scientific & Industrial Research.